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PRODUCTION OF COLORED PHOTOGRAPHIC IMAGES WITH OXODIAZOLE COUPLERS

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6 Claims. (Cl. 96—55)

The present invention relates to a process for the manufacture of colored photographic images by color development in the presence of a color coupler, to photographic developers or to photographic material which contain such color coupler, and to photographic images obtained according to this process.

It is known to obtain a colored photographic image by developing a reducible silver salt image in the presence of a color coupler, i.e. a compound which during development couples with the oxidation product of the developing agent and forms a dyestuff which precipitates onto the developed silver grains.

Magenta colored images are usually obtained by development in the presence of compounds which contain an active methylene group, for example compounds wherein the methylene group is connected at one side with a heterocyclic ring and at the other side with another group capable of activating a methylene group such as a cyan group. Such compounds are for instance oxodiazolyl-2-acetonitrile and cyano-acetyl coumarone.

Now we have found a class of compounds suited for use as color coupler, some members of which supersede the known compounds by showing higher reactivity, yielding dyes with smaller and more sharply limited absorption curves (which means more saturated colors), and yielding perfectly transparent images.

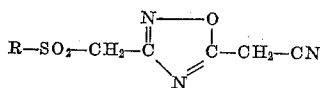
It is an object of the present invention to provide a new process for the production of colored photographic images by color development.

Another object of this invention is to provide new photographic developers containing a color coupler.

A further object is to provide new photographic material containing a color coupler.

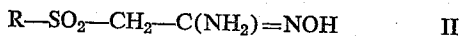
Still further objects will become apparent from the following description.

According to the present invention, a reducible silver salt image is developed with an aromatic amino developing agent in the presence of a compound according to the formula



wherein R=the radical of a hydrocarbon.

These compounds may be obtained by causing cyanoacetic acid chloride to react with amidoximes having the formula



obtained by reaction of HONH_2 with nitriles ($\text{R-SO}_2\text{-CH}_2\text{-CN}$). The latter are obtained by reaction of chloro-acetonitrile with the sodium salts of sulphonic acids ($\text{R-SO}_3\text{H}$).

The preparation of nitriles with various radicals R is described by J. Tröger and W. Hille: J. Pr. Chem. (2), 71 (1905), 225-236, and the preparation of the cor-

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responding amidoximes by J. Tröger and P. Volkmer, loc. cit., pages 236-248.

The presence of color couplers according to the present invention during color development may arise from adding to the photographic material or to the developer, a compound which differs from the color coupler only because in the active CH_2 -group one or two hydrogen atoms are replaced by a group splitting off either before development occurs by the action of the alkali in the developing solution or during the color development.

The color couplers of the present invention may be added to the developer or to a colloid layer, either to a light-sensitive silver halide emulsion layer or to a non-light-sensitive layer, adjacent to a sensitive layer or separated therefrom by a permeable colloid layer. They are, however, particularly suited for use in the developer as illustrated hereinafter.

The aromatic amino compounds, which according to the present invention are used as developing agents, comprise mono-, di- and tri-amino aryl compounds, particularly N:N-dialkyl-para-phenylene diamines and derivatives such as N:N-dialkyl-N'-sulpho- or carboxy-methyl-para-phenylene diamines.

The following examples serve to illustrate the present invention without limiting, however, the scope thereof.

EXAMPLE 1

22.8 g. (0.1 mol) p-tolulsulphonyl-acetamidoxime obtained by the method described by J. Tröger and P. Volkmer (loc. cit.) are suspended in 250 cm.³ anhydrous benzene. Whilst heating, 20.7 g. (0.2 mol) cyanoacetyl chloride are added within 15 minutes. Next, part of the benzene (about 150 cm.³) is distilled off. After cooling, the precipitate is separated by filtration and refluxed for 15 minutes in 150 cm.³ acetic acid. The reaction mixture is poured out into 1 litre water. The precipitate is sucked off and recrystallized from methanol and benzene respectively. A product, melting at 127° C. and corresponding to the Formula I wherein R=p-tolyl, is obtained.

An exposed photographic film strip, coated with a silver halied emulsion layer, is developed in a bath of the following composition:

Solution A

(NaPO ₃) ₆ -----	G.
Na ₂ SO ₃ (anhydrous) -----	1
N:N-diethyl-p-phenylene-diamine hydrochloride ---	3
Na ₂ SO ₄ (anhydrous) -----	40
Na ₂ CO ₃ (anhydrous) -----	35
KBr -----	1.5
Water to 900 cm. ³ .	

Solution B

NaOH -----	1.5
3-(p-tolylsulphonyl-methyl) - 5 - cyanomethyl-oxidiazol-1:2:4 -----	1
Water to 50 cm. ³ .	

Before use, solution B is added to solution A and water is added to the resulting solution to 1000 cm.³. The developed image is rinsed for 30 minutes and the silver is bleached in the following bath:

K ₃ Fe(CN) ₆ -----	G.
KBr -----	50
Water to 1000 cm. ³ .	3

The image is rinsed again for 10 minutes and then fixed for 20 minutes in the following bath:

Sodium thiosulphate -----	G.
Water to 1000 cm. ³ .	250

and again rinsed for 30 minutes.

A magenta image with an absorption maximum at 525 $m\mu$ is obtained.

EXAMPLE 2

Beta-naphthyl-sulphonyl-acetamidoxime, melting at 143° C., is prepared as described by J. Tröger and P. Volkmer (loc. cit.). 26.4 g. (0.1 mol) of this amidoxime are treated with 15 g. (0.15 mol) cyanoacetyl chloride in ethereal solution. After heating for 2½ hours on the waterbath, the precipitate is filtered off, washed with an aqueous solution of H_2SO_4N and next with water until neutral reaction of the wash water, boiled in a minimum of acetic acid and poured into water. A color coupler, corresponding to Formula I, wherein R=beta-naphthyl, and melting at 122–124° C., is obtained.

By exposing and further treating a film strip as in Example 1, but replacing the color coupler by that described in the present example, a magenta image with an absorption maximum at 525 $m\mu$ is obtained.

EXAMPLE 3

p-Nitrophenyl-sulphonyl-acetonitrile melting at 159–160° C. and the corresponding amidoxime melting at 195–196° C. are prepared by the same method as described by J. Tröger and P. Volkmer (loc. cit.) for beta-naphthyl-sulphonyl-aceto-amidoxime.

25.9 g. (0.1 mol) amidoxime of p-nitrophenyl-sulphonyl-aceto-nitrile are treated in anhydrous ether with 15 g. (0.15 mol) cyano acetyl chloride. The precipitate is sucked off, boiled in acetic acid, poured into water and recrystallized from methanol. A color coupler corresponding to Formula I, wherein R=p-nitrophenyl, and melting at 205–207° C., is obtained.

By exposing and further treating a film strip as in Example 1, but replacing the color coupler by that described in the present example, a magenta image with an absorption maximum at 518 $m\mu$ is obtained.

EXAMPLE 4

3-nitro-4-methylphenyl-sulphonyl-acetonitrile prepared by nitration of p-tolylsulphonyl-acetonitrile and melting at 115–116° C. is transformed into the corresponding amidoxime melting at 152° C. by the method of J. Tröger and P. Volkmer (loc. cit.). A mixture of 27.3 g. (0.1 mol) of this amidoxime, suspended in 200 cm^3 anhydrous ether, and 15 g. (0.15 mol) cyano-acetyl chloride are refluxed for 9 hours on the water bath. The precipitate is filtered off, washed with an aqueous solution of H_2SO_4N and with water, boiled in acetic acid and poured into water. After recrystallization from a mixture of water and acetone, a color coupler corresponding to Formula I, wherein R=3-nitro-4-methylphenyl, and melting at 149–150° C. is obtained.

By exposing and further treating as in Example 1, but replacing the color coupler by that described in the present example, a magenta image with an absorption maximum at 515 $m\mu$ is obtained.

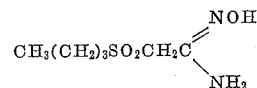
EXAMPLE 5

Chloroacetonitrile is added under reflux and in 100% excess to 60 g. of the magnesium salt of butyl sulphinic acid $(CH_3-(CH_2)_3-SO_2)_2Mg \cdot 2H_2O$, prepared according to the method of G. Houlton and H. V. Tartar: J. Amer. Chem. Soc., 60 (1938), 544–51, and suspended in 250 cm^3 $(CH_3)_2N \cdot CHO$. A perfect solution is obtained which is refluxed for 1 hour. A little precipitate is sucked off. The precipitate, obtained by diluting the filtrate with water, is extracted with ether. The extract is dried and distilled in circumstances such as 138–140° C./0.4 mm. and 148–150° C./0.6 mm. A pale yellow oil having the formula $CH_3(CH_2)_3SO_2CH_2CN$ and solidifying after a long time is obtained. Melting point: 37–39° C.

Analysis.—N calculated 8.70%; found 8.72–8.6%. S calculated 19.86%; found 20.03–20.24%.

9 g. of this product are dissolved in 150 cm^3 C_2H_5OH

and a solution of 5.8 g. $NH_2OH \cdot HCl$, and 4.5 g. Na_2CO_3 in 75 cm^3 water are added. The whole is refluxed for 45 minutes and filtered while warm on bone black. The precipitate formed after cooling is sucked off and recrystallized from a mixture of equal volumes of C_2H_5OH and benzene. A product melting at 121° C. and corresponding to the formula



is obtained.

10 g. of this amidoxime in benzene are kept with distilled cyanoacetyl chloride in 50% excess for 30 minutes at room temperature and for 1 hour at 80° C. The separated precipitate is boiled with CH_3COOH , recrystallized twice from a mixture of equal volumes of water and CH_3COOH . A product melting at 102–104° C. and corresponding to Formula I, wherein $R=CH_3-(CH_2)_3$ is obtained.

By exposing and further treating as in Example 1, but replacing the color coupler by that described in the present example, a magenta image with an absorption maximum at 510 $m\mu$ is obtained.

EXAMPLE 6

The developing solution given in Example 1 may be replaced by the following:

Solution A

	G.
Color developing substance	2
Na_2SO_3 (anhydrous)	4
Na_2CO_3 (anhydrous)	50
KBr	0.5
$(NaPO_3)_6$	1
Water to 900 cm^3 .	

Solution B

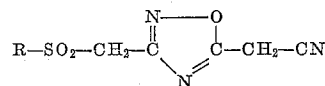
Color coupler	g-- 2
KOH	g-- 1
Ethanol	cm^3 30

Before use, solution B is added to solution A and water is added to the resulting solution to 1000 cm^3 .

By the use in this solution of the derivative, wherein $R=p$ -tolyl, as color coupler and as color developing substance of 1-(beta-methylsulphonamido-ethyl)-6-amino-tetrahydroquinoline, 1 - (delta - sulphobutylene) - 6-amino-tetrahydroquinoline, or 9-amino-julolidine, images with an absorption maximum at 535, 580, 540–545 $m\mu$ respectively are obtained.

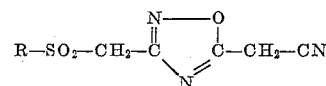
We claim:

1. A process for the production of a colored photographic image, which comprises developing a reducible silver salt image in a photographic element by means of a primary aromatic amino developing agent in the presence of a color coupler having the following formula:



wherein R represents a member selected from the group consisting of an alkyl radical and an aryl radical.

2. A process for the production of a colored photographic image, which comprises developing a reducible silver salt image in a photographic element by means of a primary aromatic amino developing agent in the presence of a color coupler having the following formula:

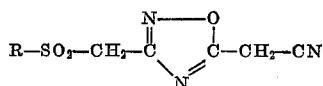


wherein R=aryl.

3. Photographic developer containing a primary aro-

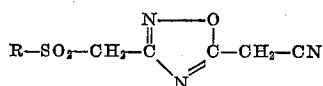
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matic amino developing agent and a color coupler having the following formula:



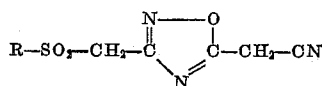
wherein R represents a member selected from the group consisting of an alkyl radical and an aryl radical.

4. Photographic developer containing a primary aromatic amino developing agent and a color coupler having the following formula: 10



wherein R=aryl.

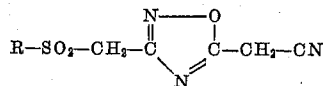
5. A photographic material comprising at least one silver halide emulsion layer, one of the layers containing a color coupler having the following formula:



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wherein R represents a member selected from the group consisting of an alkyl radical and an aryl radical.

6. A photographic material comprising at least one silver halide emulsion layer and at least one other colloid layer, one of said layers containing a color coupler having the following formula:



wherein R=aryl.

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